# A METHOD OF SOLVING SETS OF NONLINEAR ALGEBRAIC EQUATIONS

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#### FOREWARD

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Robert J. Adler

Head

Chemical Engineering Science Division

## ABSTRACT

The second generation computer program being developed as part of this research program has been applied to a problem from the field of nuclear magnetic resonance spectroscopy. The program incorporates the supplementary techniques of partitioning and some limited forms of factoring together with an improved algorithm for eliminating polynomial variables. The problem solved consisted of five multivariate polynomial equations, four nonlinear and one linear, in five variables. Twelve real solutions, which are permulations of two "true solutions," were shown to exist. The problem illustrates the capabilities of the second generation program and the usefulness of supplementary techniques.

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## INTRODUCTION

This report is the fifth semi-annual progress report made by Case
Western Reserve University under NASA Research Grant NGR-36-003-021
entitled "A Method of Solving Sets of Nonlinear Algebraic Equations."

The research seeks to develop and evaluate combined algebraic and numerical procedures for the computer solution of systems of multivariate polynomial equations. Previous Progress Reports have discussed the results
obtained with a first generation computer program and developments
underlying a second generation computer program. This report describes
the results of applying the second generation computer program now being
completed to the solution of a problem in nuclear magnetic resonance (NMR)
spectroscopy.

#### 2. PROBLEM DESCRIPTION

Through the analysis of NMR spectral data it is possible to obtain the values of certain parameters which are of considerable value to structural organic and inorganic chemists. These parameters, called chemical shifts and spin-spin coupling constants, are intimately related to the electronic and nuclear configurations of molecules. Postulated structures can often be confirmed or excluded solely from NMR spectra.

The conventional technique for analysis of NMR spectra is an iterative one, where the spin parameters are initially estimated and iteratively improved until the calculated and experimental spectra are brought into agreement. Convergence and uniqueness are usually problems. When more than one or two parameters are involved, it is difficult and costly to seek all of the possible solutions and impossible to be sure that the correct one has been found.

An alternative procedure researched by Professor Whitman<sup>2</sup> in the Chemistry Department at Case Western Reserve University consists of deducing from quantum-mechanical rules an idealized spectrum which agrees with the main features of the experimental spectrum. The spin parameters are then determined so that the calculated and idealized spectra agree precisely; in practice only the line positions are matched. In many interesting cases explicit equations are obtained for the spin parameters in terms of the experimental NMR spectral line positions. However, in several of the most interesting cases<sup>3</sup> this technique produces a system of nonlinear equations in the NMR spin parameters.

In particular, the general three-proton system (called the ABC case) yields a system of five equations—four of which are nonlinear—in the five-spin parameters  $x_1$ ,  $x_2$ ,  $x_3$ ,  $y_1$  and  $y_2$ :

$$\begin{cases} x_1 + x_2 + x_3 & = c_1 & \text{(1a)} \\ x_1 (y_1 - 2y_2) + x_2 (y_2 - 2y_1) + x_3 (y_1 + y_2) & = c_2 & \text{(1b)} \\ \frac{2}{3} (y_1^2 + y_2^2 - y_1 y_2) - \frac{3}{2} (x_1 x_2 + x_1 x_3 + x_2 x_3) & = c_3 & \text{(1c)} \\ x_1 (y_1 - 2y_2)^2 + x_2 (y_2 - 2y_1)^2 + x_3 (y_1 + y_2)^2 & = c_4 & \text{(1d)} \\ 2 (y_1 - 2y_2) (y_2 - 2y_1) (y_1 + y_2) & = c_5 & \text{(1e)} \end{cases}$$

For the specific ABC system vinyl chloride, the experimentally determined constants, which are functions of the line positions, are:

Using iterative numerical techniques, Professor Whitman found one solution.

Because of difficulty experienced in obtaining convergence, and because it was suspected that more than one solution might exist, the problem was brought to our attention.

## 3. SOLUTION BY ELIMINATION

The second generation program under development was applied to solve this problem in two different ways. In the first method of solution, only the modified van der Waerden's elimination algorithm was used. The program eliminated the variables  $x_1$ ,  $x_2$ ,  $x_3$ , and  $y_1$ , in that order, to yield a univariate polynomial of 30th degree in  $y_2$ . A first attempt to solve this final polynomial failed because of overflow. Rescaling the problem by substituting  $y_2 = 10y_2^{'}$  resolved this difficulty. Twelve real solutions were found to exist as listed in Table I.

| Set | $\mathbf{x}_1$                     | <u>x</u> 2               | <u><b>x</b></u> <sub>3</sub> | Y1                | <b>Y</b> 2       |
|-----|------------------------------------|--------------------------|------------------------------|-------------------|------------------|
| 1.  | <b>-</b> 9 <b>·</b> 28 <b>11</b> 5 | 1 • 47651                | -12 •6274                    | <b>-47.</b> 9895  | -4.23412         |
| 2.  | 1.47651                            | -12.6274                 | -9 • 28115                   | 4.23412           | -43.7554         |
| 3.  | -12.6274                           | <b>-</b> 9·2811 <b>5</b> | 1.47651                      | 43• 7554          | 47•9895          |
| 4.  | -9•28115                           | -12.6274                 | 1•47651                      | 47•9895           | 43•7554          |
| 5.  | -12.6274                           | 1.47651                  | -9•28115                     | <b>-43• 7554</b>  | 4.23412          |
| 6.  | 1•47651                            | -9.28115                 | -12•6274                     | -4.23412          | <b>-47</b> •9895 |
|     |                                    |                          |                              |                   |                  |
| 7.* | 1•45397                            | <b>-7·11</b> 808         | -14.7679                     | -2:53189          | -46•9489         |
| 8.  | <b>-7</b> • 11808                  | -14.7679                 | 1.45397                      | 46• 9489          | 44-4170          |
| 9.  | -14• 7679                          | 1•45397                  | -7•11808                     | -44• 4170         | 2•53189          |
| 10. | 1•45397                            | -14• 7679                | <b>-7• 11</b> 808            | 2• 53189          | -44• 4170        |
| 11. | -14• 7679                          | <b>-7·</b> 11808         | 1• 45397                     | 44• 4170          | 46•9489          |
| 12. | <b>-7• 118</b> 08                  | 1• 45397                 | -14•7679                     | <b>-</b> 46• 9489 | -2•53189         |

Table I Solutions to NMR Spectroscopy Problem

Solution found by Professor Whitman using iterative numerical methods.

These twelve solutions are permutations of two different sets of spin parameters. The first six solutions correspond to permutations of one set of spin parameters, while the last six are permutations of the second set. Both sets of spin parameters are in precise agreement with the observed spectral line positions. However, the two sets yield different intensities. In this particular problem the second set, which was found by Professor Whitman, more closely matches the experimental intensities. Using double-precision arithmetic, the total computing time was 535 seconds. The maximum number of list cells employed simultaneously during the computation was 1064. Together with other auxiliary data structures, the peak number of memory words employed for data storage was about 8,000 words.

## 4. SOLUTION BY SUPPLEMENTARY TECHNIQUES COMBINED WITH ELIMINATION

A second more efficient method of solution made use of the supplementary techniques of grouping and partitioning. The steps of the second solution are now described in detail. After eliminating  $\mathbf{x}_1$  and  $\mathbf{x}_2$ , the equations become:

$$\begin{cases} x_1 + x_2 + x_3 & = c_1 \\ x_1(y_1 - 2y_2) + x_2(y_2 - 2y_1) + x_3(y_1 + y_2) & = c_2 \end{cases}$$
(2a)  

$$\begin{cases} \frac{27}{2}x_3^2(y_1^2 + y_2^2 + y_1y_2) - \frac{9}{2}x_3[2c_1(y_1^2 + y_2^2 - y_1y_2) + c_2(y_1 + y_2)] \\ + \frac{3}{2}[c_2 - c_1(y_1 - 2y_2)][c_2 - c_1(y_2 - 2y_1)] \\ + 6(y_1 - y_2)^2(y_1^2 + y_2^2 - y_1y_2) & = 9c_3(y_1 - y_2)^2 \end{cases}$$
(2c)  

$$9 x_3y_1y_2 - c_1(y_1 - 2y_2)(y_2 - 2y_1) - c_2(y_1 + y_2) = c_4$$
(2d)  

$$2(y_1 + y_2)(y_1 - 2y_2)(y_2 - 2y_1) & = c_5$$
(2e)

The symmetry of Yi and y2 in the subsystem (2c), (2d) and (2e) suggested the following groups:

$$\begin{cases} P = y_1 y_2 \\ Q = y_1 + y_2 \end{cases} \tag{3}$$

Introducing P and Q into (2c), (2d) and (2e) by hand and appending system (3) to (2) yields the following partitionable system.

<sup>\*</sup>Other useful groups also exist. For example,  $P' = (y_1 - 2y_2) + (y_2 - 2y_1)$  and  $Q' = (y_1 - 2y_2)(y_2 - 2y_1)$ .

$$\begin{cases} x_1 + x_2 + x_3 & = c_1 \\ x_1 (y_1 - 2y_2) + x_2 (y_2 - 2y_1) + x_3 (y_1 + y_2) & = c_2 \end{cases}$$
(4a)

$$\begin{cases} \frac{27}{2} x_3^2 (Q^2 - 3P) - \frac{9}{2} [2c_1(Q^2 - 3P) + c_2Q] \\ + \frac{3}{2} [c_2^2 + c_1c_2Q - c_1^2(2Q^2 - 9P)] \\ + 6(Q^2 - 4P)(Q^2 - 3P) &= 9c_3(Q^2 - 4P) \end{cases}$$

$$= 9c_3(Q^2 - 4P) \qquad (4b)$$

$$9x_3P + c_1(2Q^2 - 9P) - c_2Q &= c_4$$

$$2Q(9P - 2Q^2) &= c_5$$

$$\begin{cases} P = y_1 y_2 \\ Q = y_1 + y_2 \end{cases} \tag{4c}$$

The subsystem (4b) can be solved by eliminating first  $x_3$  and then P to obtain a 12th degree polynomial in Q. This polynomial in Q has six real solutions, each of which gives rise to a  $(x_3, P, Q)$  solution to (4b). Each of these sets when substituted into (4c) yields a pair of  $(x_3, y_1, y_2, P, Q)$  solutions to (4b,c). Each of these  $(x_3, y_1, y_2, P, Q)$  solutions when substituted into (4a) yields a  $(x_1, x_2, x_3, y_1, y_2, P, Q)$  solution for the entire problem (4). All twelve of these solutions satisfy (1) and are in agreement with the solutions of Table I to at least seven significant figures.

This method of solution, employing the supplementary techniques of grouping and partitioning combined with elimination, required only 161 seconds of computing time and a peak number of list cells of 214.

## CONCLUDING REMARKS

5.

From the standpoint of NMR spectroscopy, this capability of finding all solutions, in this case a "double" solution, is of considerable importance, since many workers have neglected the possibility of multiple solutions. The method of solution being developed in this research will, among other things, be of significant practical value to NMR spectroscopists, since it will permit the analysis of NMR spectra to be performed unambiguously for ABC, ABCD, etc., systems. It should be emphasized that the method provides essentially the only means of determining the uniqueness, and thus the reliability, of spectral analyses for such systems.

The example presented is representative of the capabilities of the second generation computer program as it presently exists; approximately four nonlinear variables can be handled in typical cases by using elimination only. This example also serves to illustrate the usefulness of supplementary techniques, which can increase the size of problems that can be handled. The most critical computing factor is memory space. Propagation of round-off errors and computing time do not appear to be as critical. Further development of supplementary techniques and the availability of larger memories will permit somewhat larger problems to be treated in the future.

6 • PERSONNEL

Personnel associated with the research during the last six-month period include Professor R. J. Adler and graduate students S. Y. Ku, C. G. Sperling and W. R. Brown. Mr. Ku is a Ph.D. candidate and Messrs. Sperling and Brown are M.S. candidates. All three of these men will be writing theses during 1968.

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